Technical Paper 64

DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
VAN. H. MANNING, ACTING DIRECTOR

DETERMINATION OF NITROGEN IN COAL

A COMPARISON OF VARIOUS MODIFICATIONS OF THE KJELDAHL METHOD WITH THE DUMAS METHOD

BY

ARNO C. FIELDNER
AND
CARL A. TAYLOR

WASHINGTON
GOVERNMENT PRINTING OFFICE
1915

The Bureau of Mines, in carrying out one of the provisions of its organic act—to disseminate information concerning investigations made—prints a limited free edition of each of its publications.

When this edition is exhausted copies may be obtained at cost price only through the Superintendent of Documents, Government Printing Office, Washington, D. C.

The Superintendent of Documents *is not an official of the Bureau of Mines.* His is an entirely separate office and he should be addressed:

SUPERINTENDENT OF DOCUMENTS,
Government Printing Office,
Washington, D. C.

The general law under which publications are distributed prohibits the giving of more than one copy of a publication to one person. The cost of this publication is 5 cents.

First edition. July, 1915.

CONTENTS.

Page.
Introduction 5
General procedure in determinations 5
Results of experiments 6
  Series 1, determinations by Kjeldahl method 6
  Series 2, determinations by Kjeldahl-Gunning method 7
  Series 3, determinations showing effect of various concentrations of potassium sulphate 9
  Series 4, determinations by Kjeldahl-Gunning-Jodlbauer method 10
  Series 5, determinations by Gunning method 11
  Series 6, determinations by copper-sulphate modification of Kjeldahl method 12
  Series 7, determinations by Wilfarth's modification with the use of P_2O_5 13
  Series 8, determinations by Dumas method 14
    Procedure 14
    Testing the method 15
    Experimental work 16
  Conclusions from experiments 18
Summary 21
Acknowledgment 22
Publications on fuel technology 23

TABLES.

Page.
TABLE 1. Sources and classes of coals used in nitrogen determinations 5
2. Results of determination of nitrogen in various coals by the Kjeldahl method 7
3. Results of determinations of nitrogen in various coals by the Kjeldahl-Gunning method 8
4. Results of nitrogen determinations showing effect of varying amounts of K_2SO_4 in Kjeldahl-Gunning method 10
5. Results of nitrogen determinations by the Kjeldahl-Gunning-Jodlbauer method 11
6. Results of nitrogen determinations by the Gunning method 12
7. Results of nitrogen determinations by the copper-sulphate modification of the Kjeldahl method 13
8. Results of nitrogen determinations by Wilfarth's modification with the use of P_2O_5 14
9. Results of experiments to determine quantity of nitrogen given off from copper oxide on heating under various conditions 18
10. Comparative results of nitrogen determinations by Dumas and by Kjeldahl-Gunning method 20

Original from PRINCETON UNIVERSITY

ILLUSTRATIONS.

Page.

FIGURE 1. Curves showing results of determination of nitrogen in various coals by the Kjeldahl method with and without the use of potassium permanganate 6

2. Curves showing the results of determination of nitrogen in various coals by the Kjeldahl-Gunning method 8

3. Curves showing comparative results of determinations of nitrogen in various coals by the Kjeldahl and by the Kjeldahl-Gunning methods 9

4. Curves showing comparative results of determinations of nitrogen in various coals by various methods 11

5. Curves showing comparative results of determinations of nitrogen in various coals by the Dumas and by the Kjeldahl-Gunning method 20

DETERMINATION OF NITROGEN IN COAL; A COMPARISON OF VARIOUS MODIFICATIONS OF THE KJELDAHL METHOD WITH THE DUMAS METHOD.

By Arno C. Fieldner and Carl A. Taylor.

INTRODUCTION.

The experiments described in this paper were undertaken in the course of fuel investigations being made by the Bureau of Mines, their purpose being to ascertain which modifications of the Kjeldahl method are best adapted to the determination of nitrogen in coal, and, if possible, to check the results with the Dumas gas-volumetric method. The latter method, although difficult and tedious, is generally regarded as being applicable to almost all classes of organic compounds.

In a series of determinations some of the best known of the various modifications of the Kjeldahl method were used. Eight coals were chosen to represent various types ranging in nitrogen content from 0.8 to 1.8 per cent. The sources and classes of the coals used are given in Table 1 following.

Table 1.—*Sources and classes of coals used in nitrogen determinations.*

Coal No.	Source.	Bed.	Class.
1	Morton County, N. Dak.		Lignite.
2	Musselshell County, Mont		Subbituminous.
3	Bureau County, Ill.	No. 3	Bituminous.
4	New River field, W. Va.	Sewell	Semibituminous.
5	McDowell County, W. Va.	Pocahontas No. 3.	Do.
6	Allegany County, Md.	Davis 6-foot	Do.
7	Fayette County, W. Va.	Sewell	Do.
8	Campbell County, Tenn.	Rex	Bituminous.

GENERAL PROCEDURE IN DETERMINATIONS.

A considerable quantity of each sample was prepared by pulverizing the air-dried coal in a porcelain ball mill to pass a 60-mesh sieve, and most of the material would pass through a 100-mesh sieve.

The general procedure in all of the Kjeldahl methods was essentially as follows: A 1-gram sample was digested in a 550-c. c. Kjeldahl flask with 30 c. c. of concentrated sulphuric acid and the other reagents required in the particular modification being used. The flask was first heated over a low flame till frothing subsided and then at a temperature sufficient to cause gentle ebullition. The digestions were continued for definite periods of time—two, three, four, and seven hours in the various series. In those determinations in which potassium permanganate was used, it was added in the form of powder or small crystals, about 10 minutes after the flame had been extinguished. The mixture had then cooled enough so that the violent local action that takes place when permanganate is added to the boiling mixture was avoided. Adding permanganate under these conditions several times during digestion did not cause appreciable loss of nitrogen, a result confirming that obtained by Siegfried and Weidenhaupt.[a] After the solution had been cooled and diluted to 250 c. c., a few grams of granulated zinc and an excess of sodium-hydroxide solution containing potassium sulphide were added and the flask at once connected to a block-tin condenser. To avoid the mechanical carrying over of alkali, the distillation was conducted very slowly—at the rate of 150 c. c. in 1½ to 2 hours. The ammonia was collected in standard sulphuric-acid solution and titrated with a standard ammonia solution, cochineal being the indicator. The solutions were carefully standardized by several methods. Blank determinations were made in all cases, 1 gram of pure sucrose being used in place of the coal sample.

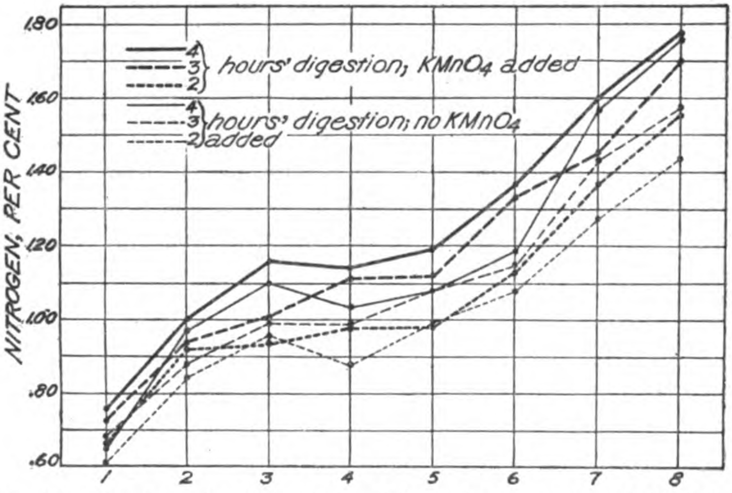

FIGURE 1.—Curves showing results of determination of nitrogen in various coals by the Kjeldahl method with and without the use of potassium permanganate. Numbers on ordinates represent coals similarly numbered in Table 1.

RESULTS OF EXPERIMENTS.

SERIES 1, DETERMINATIONS BY KJELDAHL METHOD.

Table 2 and the curves in figure 1 show the results obtained by digesting the samples with 30 c. c. of concentrated sulphuric acid and 0.7 gram of mercury for periods of two, three, and four hours, both with and without the addition of potassium permanganate after the digestion had been completed. An inspection of the plotted results shows clearly that the amount of nitrogen obtained increases with the time of digestion and with the addition of permanganate. Seemingly this method requires more than four hours' digestion to insure the maximum yield of nitrogen.

---

[a] Siegfried, Max., and Weidenhaupt, O., Zur Methode Kjeldahls: Ztschr. physiol. Chem., Jahrg. 76, 1912, s. 238.

TABLE 2.—*Results of determination of nitrogen in various coals by the Kjeldahl method.*

[Digestion with 0.7 gram Hg and 30 c. c. H_2SO_4.]

Coal No.[a]	Determination No.	No $KMnO_4$ added at end of digestion. Percentage of nitrogen after digestion for—			$KMnO_4$ added at end of digestion. Percentage of nitrogen after digestion for—			Number of hours of digestion before liquid became colorless.
		Two hours.	Three hours.	Four hours.	Two hours.	Three hours.	Four hours.	
1	1	0.63	0.68	0.65	0.65	0.70	0.75	1¾
	2	.60	.68	.63	.66	.75	.75	
	3			.66	.65			
	4			.68	.70			
	Average	.61	.68	.65	.66	.73	.75	
2	1	.83	.89	.98	.91	1.01	1.01	2
	2	.85	.88	.97	.93	.93	1.01	
	3					.93		
	4					.91		
	5					.92		
	Average	.84	.88	.97	.92	.94	1.01	
3	1	.93	1.03	1.13	.95	1.02	1.16	2
	2	1.00	.95	1.08	.90	1.04	1.15	
	3					1.00		
	Average	.96	.99	1.10	.93	1.02	1.16	
4	1	.91	1.01	1.04	.99	1.10	1.15	1¾
	2	.89	.98	1.04	.98	1.16	1.13	
	3	.86				1.09		
	4					1.12		
	Average	.88	.99	1.04	.98	1.12	1.14	
5	1	.98	1.10	1.10	1.00	1.10	1.18	2
	2	1.00	1.05	1.08	.95	1.15	1.20	
	Average	.99	1.08	1.09	.98	1.13	1.19	
6	1	1.09	1.19	1.21	1.16	1.35	1.36	2¼
	2	1.08	1.13	1.18	1.08	1.36	1.38	
	3	1.06	1.15		1.15	1.33		
	4					1.31		
	Average	1.08	1.15	1.19	1.13	1.34	1.37	
7	1	1.26	1.45	1.55	1.39	1.48	1.58	2
	2	1.29	1.43	1.60	1.36	1.45	1.63	
	Average	1.28	1.44	1.58	1.37	1.46	1.60	
8	1	1.40	1.53	1.75	1.56	1.75	1.79	2¼
	2	1.47	1.58	1.78	1.54	1.67	1.78	
	3	1.45	1.63		1.58	1.65		
	4					1.65		
	5					1.78		
	Average	1.44	1.58	1.76	1.56	1.70	1.78	

[a] For a description of the coals see Table 1.

SERIES 2, DETERMINATIONS BY KJELDAHL-GUNNING METHOD.

Table 3 and the curves in figure 2 show the results obtained by digesting the samples with 30 c. c. of concentrated sulphuric acid, 0.7 gram of mercury, and 7 grams of potassium sulphate for periods of two, three, four, and seven hours, with and without the addition of permanganate at the end of digestion.

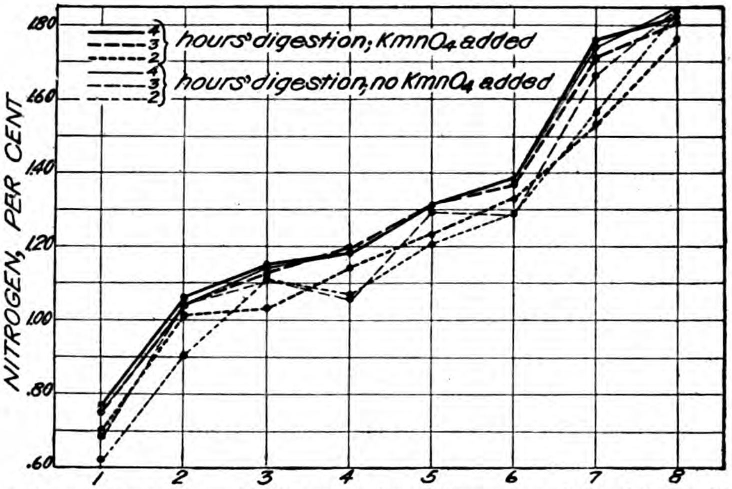

FIGURE 2.—Curves showing the results of determination of nitrogen in various coals by the Kjeldahl-Gunning method. Numbers on ordinates represent coals similarly numbered in Table 1.

TABLE 3.—*Results of determinations of nitrogen in various coals by the Kjeldahl-Gunning method.*

[Digestion with 0.7 gram Hg and 30 c. c. H_2SO_4.]

Coal No.[a]	Determination No.	No $KMnO_4$ added.			$KMnO_4$ added at end of digestion.				Number of hours of digestion before liquid became clear.
		Percentage of nitrogen after digestion for—			Percentage of nitrogen after digestion for—				
		Two hours.	Three hours.	Four hours.	Two hours.	Three hours.	Four hours.	Seven hours.	
1	1	0.61	0.66	0.71	0.68	0.78	0.78	0.80	1¼
	2	.64	.69	.76	.71	.77	.76	.78	
	3				.71	.71			
	4					.74			
	Average	.63	.68	.74	.70	.75	.77	.79	
2	1	.91	1.05	1.05	.99	1.05	1.07	1.05	1½
	2	.91	1.03	1.04	1.03	1.04	1.05	1.07	
	3					1.04			
	Average	.91	1.04	1.04	1.01	1.04	1.06	1.06	
3	1	1.12	1.12	1.13	.98	1.15	1.15	1.18	1¾
	2	1.10	1.10	1.15	1.07	1.13	1.15	1.16	
	3				1.04	1.12			
	Average	1.11	1.11	1.14	1.03	1.13	1.15	1.17	
4	1	1.08	1.19	1.19	1.15	1.16	1.18	1.15	1½
	2	1.06	1.16	1.19	1.14	1.22	1.20	1.16	
	3		1.14		1.17	1.24	1.18		
	4				1.12	1.19			
	5					1.17			
	Average	1.07	1.16	1.19	1.14	1.20	1.19	1.16	
5	1	1.19	1.29	1.31	1.26	1.31	1.31	1.20	1¾
	2	1.23	1.31	1.30	1.21	1.31	1.31	1.33	
	3							1.25	
	Average	1.21	1.30	1.31	1.24	1.31	1.31	1.27	
6	1	1.28	1.33	1.40	1.33	1.36	1.38	1.35	1¾
	2	1.32	1.33	1.38	1.32	1.38	1.40	1.36	
	3	1.28			1.33		1.38		
	4				1.32				
	5				1.34				
	Average	1.29	1.33	1.39	1.33	1.37	1.39	1.36	
7	1	1.62	1.67	1.73	1.57	1.72	1.77	1.66	1½
	2	1.51	1.65	1.75	1.49	1.71	1.75	1.63	
	3							1.61	
	4							1.70	
	Average	1.57	1.66	1.74	1.53	1.72	1.76	1.67	
8	1	1.85	1.83	1.86	1.75	1.76	1.83	1.87	1½
	2	1.80	1.85	1.84	1.75	1.84	1.85	1.86	
	3				1.78	1.85	1.82	1.89	
	4						1.80		
	5						1.83		
	Average	1.83	1.84	1.85	1.76	1.82	1.83	[b] 1.87	

[a] For a description of the coals see Table 1.

[b] Coal 8 digested in the same set for 4 hours gave 1.86, 1.88, and 1.86 per cent nitrogen.

The addition of potassium sulphate to the sulphuric acid and mercury accelerated the oxidation of the coal, the digestion mixture becoming colorless approximately one-half hour sooner than in series 1. In those determinations in which permanganate was used at the end of the digestion, practically identical results were obtained in the three, four, and seven hour periods. After digestion had continued for eight hours, the addition of permanganate did not change the nitrogen percentage; however, after digestion for three hours, without the use of permanganate, several low yields were obtained. Hence, adding permanganate according to the method previously described in this paper proved a positive aid to complete oxidation in those cases where the time of digestion was not quite sufficient. In no case did the addition of permanganate seem to cause any loss of nitrogen.

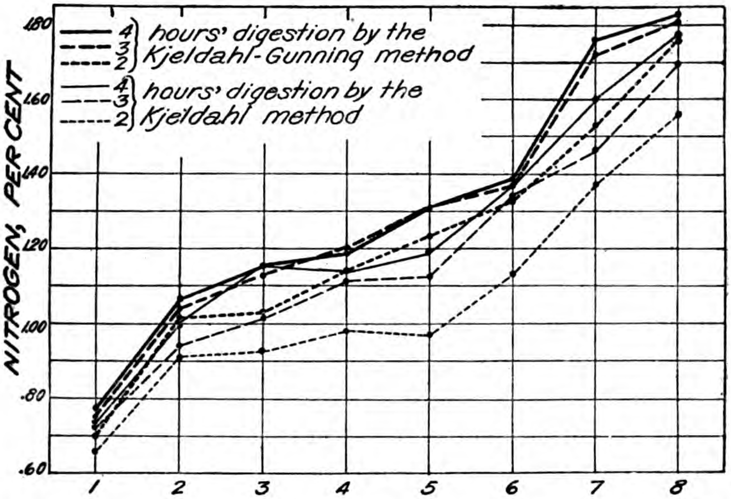

FIGURE 3.—Curves showing comparative results of determinations of nitrogen in various coals by the Kjeldahl and by the Kjeldahl-Gunning methods. Numbers on the ordinates represent coals similarly numbered in Table 1.

The greater efficiency of the Kjeldahl-Gunning method as compared with the Kjeldahl method is graphically shown in figure 3, which gives a comparison of the nitrogen yields obtained by the two methods on digestion for two, three, and four hours.

SERIES 3. DETERMINATIONS SHOWING EFFECT OF VARIOUS CONCENTRATIONS OF POTASSIUM SULPHATE.

Self[a] and Carpiaux[b] have recently called attention to the danger of volatilization of ammonia during digestion when the composition of the residue approximates that of acid potassium sulphate ($KHSO_4$). Losses of this nature were avoided by using a large excess of sulphuric acid—30 c. c. of acid to 7 grams of potassium sulphate. As shown in the results presented in Table 4, no appreciable diminution in the yield of nitrogen occurred when the potassium sulphate was increased to 15 grams. When digestion was continued four hours with 22 grams of potassium sulphate, losses of 0.04 to 0.13 per cent nitrogen took place. Seemingly, the ratio of grams of potassium sulphate to cubic centimeters of sulphuric acid should not exceed 0.5.

---

[a] Self, P. A. W., An unrecognized source of error in the Kjeldahl-Gunning method for the determination of nitrogen: Pharm. Jour., vol. 88, 1912, pp. 384–385.

[b] Carpiaux, E., A source of error in the Kjeldahl-Gunning process: Bull. Soc. chim. Belg., vol. 27, 1913, pp. 13–14.

TABLE 4.—*Results of nitrogen determinations showing effect of varying amounts of K_2SO_4 in Kjeldahl-Gunning method.*

[30 c. c. H_2SO_4, 0.7 gram. Hg, K_2SO_4 as shown, and $KMnO_4$ used at end of digestion.]

Coal No.[a]	Nitrogen obtained after digestion for three hours with—			Nitrogen obtained after digestion for four hours with 22 grams K_2SO_4.
	7 grams K_2SO_4.	10 grams K_2SO_4.	15 grams K_2SO_4.	
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
1	0.77	0.79	0.79	....
2	1.04	1.04	1.05	....
3	1.13	1.14	1.14	....
4	1.20	1.18	1.15	....
5	1.31	1.31	1.32	[b] 1.21 1.19
6	1.37	1.40	1.40	....
7	1.72	1.72	1.72	[c] 1.66 1.68 1.68
8	1.82	1.82	1.82	1.76

[a] For a description of the coals see Table 1.
[b] Coal 5 digested in the same set with 7 grams K_2SO_4 gave 1.32 per cent N.
[c] Coal 7 digested in the same set with 7 grams K_2SO_4 gave 1.72 per cent N.

SERIES 4, DETERMINATIONS BY KJELDAHL-GUNNING-JODLBAUER METHOD.

Table 5 and figure 4 give the results obtained by digesting the coal with 30 c. c. of sulphuric acid, 7 grams of potassium sulphate, 0.7 gram of mercury, 2 grams of zinc dust, and 2 grams of salicylic acid, according to the Jodlbauer modification for nitric nitrogen. The time of digestion was necessarily longer on account of the slow and gradual heating required by this method. The results after digestion for four and one-half hours were approximately the same, within the experimental error, as obtained with the standard Kjeldahl-Gunning method, being the results presented in the discussion of series 2 in which the average percentages of nitrogen for each coal in that series were determined by digestion for four hours with 30 c. c. of concentrated H_2SO_4, 0.7 gram Hg, and 7 grams K_2SO_4, $KMnO_4$ being added at the end of the digestion. As anticipated, the samples showed no nitric nitrogen.

TABLE 5.—*Results of nitrogen determinations by the Kjeldahl-Gunning-Jodlbauer method.*

[30 c.c. H_2SO_4, 7 grams K_2SO_4, 0.7 gram Hg, 2 grams zinc dust, and 2 grams salicylic acid used.[a]]

Coal No.[b]	Determination No.	Percentage of nitrogen after heating for— Three hours.	Four hours.	Four and one-half hours.	Percentage of nitrogen by standard Kjeldahl-Gunning method.	Difference.
1	1	0.75	0.75	0.78	0.77	+0.01
	2	.78	.75	.78		
	Average	.76	.75	.78		
2	1	.94	.98	.98	1.06	− .08
	2	.93	.98	.98		
	Average	.93	.98	.98		
3	1	1.12	1.15	1.17	1.15	+ .02
	2	1.07	1.12	1.16		
	Average	1.10	1.13	1.17		
4	1	1.18	1.25	1.20	1.19	.00
	2	1.25	1.23	1.18		
	Average	1.21	1.24	1.19		
5	1	1.24	1.34	1.37	1.31	+ .04
	2	1.27	1.39	1.34		
	Average	1.25	1.37	1.35		
6	1	1.15	1.28	1.30	1.39	− .08
	2	1.15	1.25	1.33		
	Average	1.15	1.26	1.31		
7	1	1.62	1.74	1.77	1.76	.00
	2	1.64	1.74	1.75		
	Average	1.63	1.74	1.76		
8	1	1.60	1.75	1.80	1.83	− .02
	2	1.65	1.80	1.82		
	Average	1.62	1.77	1.81		

[a] All of the solutions became colorless after digestion had been carried on for two hours.
[b] For a description of the coals see Table 1.

SERIES 5, DETERMINATIONS BY GUNNING METHOD.

Table 6 and figure 4 show the results obtained by digesting the coal four hours with 30 c. c. of sulphuric acid and 7 grams of potassium sulphate, according to the Gunning method, and adding potassium

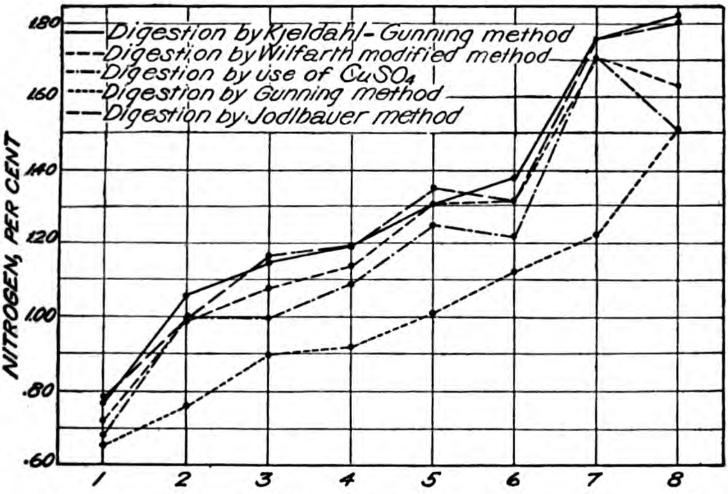

FIGURE 4.—Curves showing comparative results of determinations of nitrogen in various coals by various methods. Numbers on ordinates represent coals similarly numbered in Table 1.

permanganate at the end of digestion. This mixture oxidized the coal very slowly; from three to four hours of digestion was required before the solutions became colorless. All the results were low.

TABLE 6.—*Results of nitrogen determinations by the Gunning method.*

[30 c. c. H_2SO_4 and 7 grams K_2SO_4 used; $KMnO_4$ added at end of digestion.]

Coal No.[a]	Determination No.	Percentage of nitrogen after digestion for 4 hours.	Percentage of nitrogen by standard Kjeldahl-Gunning method.	Difference.
1	1	0.65	0.77	−0.12
	2	.65		
	Average	.65		
2	1	.78	1.06	− .30
	2	.75		
	Average	.76		
3	1	.88	1.15	− .25
	2	.93		
	Average	.90		
4	1	.90	1.19	− .26
	2	.95		
	Average	.93		
5	1	1.03	1.31	− .30
	2	1.00		
	Average	1.01		
6	1	1.10	1.39	− .26
	2	1.15		
	Average	1.13		
7	1	1.25	1.76	− .53
	2	1.20		
	Average	1.23		
8	1	1.55	1.83	− .32
	2	1.48		
	Average	1.51		

[a] For a description of the coals see Table 1.

SERIES 6, DETERMINATIONS BY COPPER-SULPHATE MODIFICATION OF KJELDAHL METHOD.

Table 7 and figure 4 show the results obtained by digesting coal three hours with 30 c. c. of sulphuric acid, 7 grams of potassium sulphate, and 1 gram of copper sulphate, and adding potassium permanganate at the end of digestion. The copper sulphate proved a less effective catalytic agent than mercury, about 45 minutes' more time being required to attain a colorless solution. The percentages of nitrogen obtained on digestion for three hours were from 0.02 to 0.37 per cent less than by the use of mercury. Longer periods of digestion would probably have given the full yield of nitrogen.

Original from PRINCETON UNIVERSITY

Table 7.—*Results of nitrogen determinations by the copper-sulphate modification of the Kjeldahl method.*

[30 c. c. H_2SO_4, 7 grams K_2SO_4, and 1 gram $CuSO_4$ used; $KMnO_4$ added at end of digestion.]

Coal No.[a]	Determination No.	Percentage of nitrogen after digestion for 3 hours.	Percentage of nitrogen by standard Kjeldahl-Gunning method.	Difference.
1	1	0.69	0.77	−0.09
	2	.68		
	Average	.68		
2	1	1.02	1.06	− .06
	2	.99		
	Average	1.00		
3	1	1.04	1.15	− .15
	2	.97		
	Average	1.00		
4	1	1.10	1.19	− .10
	2	1.08		
	Average	1.09		
5	1	1.24	1.31	− .06
	2	1.27		
	Average	1.25		
6	1	1.22	1.39	− .17
	2	1.22		
	Average	1.22		
7	1	1.69	1.76	− .06
	2	1.72		
	Average	1.70		
8	1	1.50	1.83	− .32
	2	1.53		
	Average	1.51		

[a] For a description of the coals see Table 1.

SERIES 7, DETERMINATIONS BY WILFARTH'S MODIFICATION WITH THE USE OF P_2O_5.

Table 8 and figure 4 show the results obtained by digesting the samples three hours with 30 c. c. of sulphuric acid, 6 grams of phosphorus pentoxide, and 0.7 gram of mercury, and adding potassium permanganate at the end of digestion, according to one of the Wilfarth modifications of the Kjeldahl method.

When the proportions of reagents mentioned were used, the phosphorus pentoxide was slightly less effective than potassium sulphate, and, furthermore, it is a less convenient material to use.

TABLE 8.—*Results of nitrogen determinations by Wilfarth's modification with the use of* P_2O_5.

[30 c. c. H_2SO_4, 6 grams P_2O_5, and 0.7 gram Hg used, with $KMnO_4$ added at end of digestion.]

Coal No.[a]	Determination No.	Percentage of N after digesting 3 hours.	Percentage of N by standard Kjeldahl-Gunning method.	Difference.
1	1	0.73	0.77	−0.05
	2	.71		
	Average	.72		
2	1	1.01	1.06	− .07
	2	.98		
	Average	.99		
3	1	1.11	1.15	− .07
	2	1.06		
	Average	1.08		
4	1	1.13	1.19	− .05
	2	1.16		
	Average	1.14		
5	1	1.28	1.31	.00
	2	1.33		
	Average	1.31		
6	1	1.33	1.39	− .08
	2	1.28		
	Average	1.31		
7	1	1.68	1.76	− .05
	2	1.73		
	Average	1.71		
8	1	1.63	1.83	− .20
	2	1.63		
	Average	1.63		

[a] For a description of the coals see Table 1.

SERIES 8, DETERMINATIONS BY DUMAS METHOD.

The Dumas gas-volumetric method of determining nitrogen is generally regarded as reliable and as being applicable to most classes of organic compounds. So, in making an investigation of various modifications of the Kjeldahl method of determining nitrogen in coal, it seemed desirable to check the results by determinations by the Dumas method.

PROCEDURE.

In general, the procedure followed was that given by Gattermann [a] and by Meyer,[b] an open tube being used, and pure CO_2 [c] being generated by K_2CO_3 solution and dilute H_2SO_4.[d] The combustion tube was of fused silica, and the nitrogen was collected in a Schiff nitrometer and transferred, for measurement over water, to a water-jacketed gas burette. The tube was charged in the usual manner with a roll of reduced copper gauze, 8 cm. long, and about 40 cm. of coarse CuO, followed by 50 grams of fine CuO mixed with the sample. In filling the silica tube, pouring the fine CuO around a glass rod and then removing the rod, the tube being held horizontal, thereby leaving a channel across the fine material, was found more satisfactory than to open the channel by tapping the tube, as the tapping tended to form a canal over the coarse oxide also. The fine oxide was reoxidized by being heated in the air in an iron dish after each determination. The coarse oxide was similarly treated as often as it showed any appreciable signs of reduction.

---

[a] Gattermann, Ludwig, Practical methods of organic chemistry; 1907, p. 85.

[b] Meyer, H., Analyse und Konstitutionsermittelung organische Verbindungen, Berlin, 1909, p. 185.

[c] Blau, Fritz, Verfahren zur Bestimmung des Stickstoffes in organischen Substanzen, 1892, p. 277.

[d] Young, G., and Caudwell, B. An improved apparatus for generating CO_2: Jour. Soc. Chem. Ind., vol. 26, 1907, p. 184.

TESTING THE METHOD.

To test the method a blank determination was made, 1 gram of pure sucrose supplied by the Bureau of Standards for calorimeter standardization being used. There was little difficulty in clearing the cold tube of air so that the CO_2 was completely absorbed. However, when the copper oxide, especially that part of the tube containing the fine oxide and sucrose, was heated, fine bubbles of a nonabsorbable gas began to collect in the nitrometer. At the end of two hours' heating 2 c. c. of gas had collected, and after four hours there was over 4 c. c., and the gas was coming slowly but steadily. As the sucrose and the CO_2 were both free from nitrogen, the CuO was regarded as the probable source of error.

After the furnace had cooled, the CuO was removed and ignited in the iron dish over a Chaddock burner for several hours. The Chaddock burner gave a more diffused heat than the Meker, so that the iron dish was not oxidized sufficiently to scale off iron oxide. The tube was recharged as before except that no combustible material was used. As before, the tube was cleared of air with little difficulty, but when the copper oxide was heated, a nonabsorbable gas was given off. At the end of 6 hours, 6.6 c. c. had collected. The tube containing CO_2 was allowed to cool overnight, and again heated 7 hours the next day, an additional 1.4 c. c. being yielded. At the end of the second day the evolution had practically ceased. An analysis of the gas evolved showed 5.41 per cent oxygen, a trace of combustible material, and 94.6 per cent nitrogen. The experiments were repeated, several different brands of copper oxide being used, but essentially similar results were obtained. However, oxidized copper wire seemed better than other forms as the tube was more easily cleared of air. Repeated evacuation of the cold tube with a Geryk pump and refilling with CO_2 aided in removing the air, but failed materially to reduce the gas obtained in heating.

It appeared that copper oxide prepared by igniting and cooling in the air as usually directed retained air which could not be removed by evacuating the cold tube, and which was slowly but persistently given off on heating in an atmosphere of CO_2.

A review of the literature on this subject disclosed the following references: In speaking of the Dumas method, Meyer[a] states: "The chief source of error lies in the impossibility of freeing the fine copper oxide from air, and therefore most of the results are too high by 0.1 to 0.2 per cent." Fresenius[a] states: "The results are generally somewhat too high, namely, by about 0.2 to 0.5 per cent; and that in a blank experiment with sugar the quantity of unabsorbed gas should not exceed 1 or 1.5 c. c."

---

[a] Meyer, H., Op. cit., p. 187.

Abegg and Auerbach[b] state that "black copper oxide has the power of holding gases as carbon dioxide, oxygen, nitrogen, carbon monoxide, water vapor, etc. This may be by absorption, solubility in the amorphous phase, or perhaps by chemical combination."

Morse[c] prepares both coarse and fine copper oxide for use by first heating them for 1½ hours or more at a full-red heat in a combustion tube through which is passed a current of oxygen or air. Without cooling, carbon dioxide is then passed through the tube for an hour or more. The oxide is allowed to cool in carbon dioxide.

Phillips[d] in describing the Dumas method for the determination of nitrogen in natural gas, comments as follows:

> Some difficulty was experienced in expelling air from copper oxide when the apparatus was being prepared for work. In beginning a series of determinations several days were often required for the purpose. The porcelain tube was strongly heated, while a slow stream of carbon dioxide was maintained; the CuO was not considered to be in proper condition until the escaping CO_2 was absorbed without residue. It was found that the CuO when once impregnated with CO_2, while strongly heated, could be reoxidized by air current with little tendency to occlusion of air, but if the copper oxide was allowed to cool in contact with air much time was lost in removing the air by carbon dioxide even when strong heat was applied.

As the preliminary determinations confirmed Phillips's observations in regard to the long time necessary to expel the air from copper oxide by merely heating it in a current of CO_2, it seemed desirable to try to shorten the time by heating the CuO in a vacuum before using it. Experiments were made to test the advisability of this procedure and to obtain some data tending to show how the nitrogen is held.

EXPERIMENTAL WORK.

As a basis of comparison the gas volume in each determination was reduced to the corresponding volume at 25° C. and 740 mm. pressure, which were about the average temperatures and pressure at which the experiments were made.

Experiment 1a.—In experiment 1*a*, 100 grams of Baker & Adamson's CuO fine enough to pass a 100-mesh sieve (86 per cent passed through 200-mesh), followed by a reduced-copper spiral for removing oxygen, was placed in the silica tube of a combustion furnace. The

---

[a] Fresenius (translated by Cohen), Quantitative chemical analysis, vol. 2, 6th ed., 1904, p. 68.

[b] Abegg, R., and Auerbach, Fr., Handbuch der anorganische Chemie, vol. 2, 1908, p. 604.

[c] Morse, H. N., Exercises in quantitative chemistry, 1905, p. 276.

[d] Phillips, F. C., Fluctuation in the composition of natural gas: Proc. Eng. Soc. Western Pa., vol. 14, 1898, p. 299.

Original from PRINCETON UNIVERSITY

tube was connected with a nitrometer, an apparatus for generating pure CO_2, and a Geryk pump. The air was removed by the Geryk pump and replaced by pure CO_2 several times, till there was complete absorption on passing CO_2 through the tube. The CuO was then heated to a full-red heat for two hours, resulting in the evolution of 2.5 c. c. of nonabsorbable gas.

Experiment 2a.—In experiment 2*a*, heating of the CuO used in experiment 1*a* was continued several hours, a vacuum being applied repeatedly and the gas being replaced by CO_2 until no further nonabsorbable gas was liberated. The CuO was cooled in CO_2, then removed from the tube, and let stand overnight in the air. It was then replaced in the tube and the air replaced by CO_2 by use of vacuum until there was complete absorption in KOH solution. After the CuO had been heated for two hours 2.2 c. c. of gas was collected.

Experiment 3a.—In experiment 3*a*, heating in a vacuum was continued for several hours; CO_2 was then admitted, and the tube allowed to cool. When the tube had become cool the CuO was exposed to air for two hours in an open dish, and the experiment was repeated as in experiment 1*a*; 1.9 c. c. of nonabsorbable gas or nitrogen was produced.

Experiment 4a.—In experiment 4*a*, the CuO from experiment 3*a* was cooled in CO_2, then removed from the tube, mixed with sucrose, replaced in the tube, and largely reduced to metallic copper by heating. It was then removed from the tube, again oxidized in the air as usual, replaced in the tube, and treated as in experiment 1*a*. After 2 hours' heating 3.5 c. c. of nitrogen was collected.

Experiment 1b.—In experiment 1*b*, a fresh sample of the brand of copper oxide used in experiment 1*a* was taken and treated exactly as in experiment 1*a*, the yield of nitrogen being 2.3 c. c.

Experiment 4b.—In experiment 4*b*, the CuO from experiment 1*b* was reduced with sucrose and treated exactly as in experiment 4*a*, the yield of nitrogen being 3.9 c. c.

Experiment 1c.—In experiment 1*c* 100 grams of the CuO used in experiment 4*b* was treated exactly as was the oxide in experiments 1*a* and 1*b*, 0.9 c. c. of nitrogen being obtained. In order to show the effect of the size of the CuO particles on the amount of nitrogen retained, a sample of Baker's CuO in "wire form" was pulverized to pass through a 40-mesh screen and remain on 100-mesh.

Experiment 2c.—In experiment 2*c* the oxide from experiment 1*c* was treated exactly as was the oxide in experiment 2*a*, 0.7 c. c. of nitrogen being obtained.

Experiment 4c.—In experiment 4*c* the oxide from experiment 2*c* was reduced with sucrose and treated exactly as was the oxide in experiments 4*a* and 4*b*, 2.7 c. c. of nitrogen being obtained.

Experiment 5c.—In experiment 5*c*, the oxide from experiment 4*c* was treated as a fresh sample, as was the oxide in experiments 1*a*, 1*b*, and 1*c*, 0.7 c. c. of nitrogen being obtained.

Experiment 6c.—In experiment 6*c*, the CuO from experiment 5*c* was again reduced with sucrose and further treated as was the oxide in experiments 4*a*, 4*b*, and 4*c*, and gave 3.2 c. c. of nitrogen.

Experiment 7.—In experiment 7, 60 grams of the 40 to 100 mesh material that had been reduced and reoxidized in air was tested in a special apparatus of glass and quartz with mercury seals at the joints. The CuO was placed in a quartz tube, which then was completely evacuated with a mercury pump. Heat was applied by an electric furnace, and the temperature of the CuO was raised to 800° C. Over 150 c. c. of gas was collected. This was analyzed, showing 89.60 per cent CO_2, air 8.34 per cent, excess N_2 2.06 per cent. The CuO was then removed from the apparatus and heated in air in the open dish for three hours, and again tested as described, giving less than 1 c. c. of gas under the combined heating and vacuum treatment. The same CuO after having been reduced by sucrose and cooled in CO_2 was again heated in the special apparatus in a vacuum to about 500° C., when such a large quantity of gas was suddenly evolved that the apparatus was broken and further tests discontinued.

CONCLUSIONS FROM EXPERIMENTS.

A study of the results of experiments 1 to 6, inclusive, as shown in Table 9 tends to show that the nitrogen given off on heating CuO in a vacuum or in CO_2 is held by the oxide in two ways, as follows: (1) In some form of chemical combination which takes place when reduced copper is oxidized in air; (2) by adsorption.

TABLE 9.—*Results of experiments to determine quantity of nitrogen given off from copper oxide on heating under various conditions.*

Experiment No.	Method of treatment.	Quantity of nitrogen, at 25° C. and 740 mm. pressure, given off on heating 100 grams of copper oxide at approximately 850° C. for a period of two hours.		
		Baker & Adamson 200-mesh CuO.		J. T. Baker's "wire form" 40 to 100 mesh CuO.
		Sample A.	Sample B.	Sample C.
		C. c.	*C. c.*	*C. c.*
1	Copper oxide placed in silica tube, tube evacuated, and air replaced with CO_2 repeatedly until no further nitrogen was evolved. It was then heated for two hours	2.5	2.3	0.9
2	Copper oxide from previous experiment subjected alternately to vacuum and CO_2 while heated to 850° C. for several hours, then cooled in CO_2, exposed to air 18 hours, and tested as in experiment 1	2.2	....	.7
3	CuO from previous experiment treated as in experiment 2, except exposed to air only two hours	1.9	....	....
4	CuO from preceding experiment cooled in CO_2, reduced to metallic Cu, reoxidized, cooled in air, and treated as in experiment 1	3.5	3.9	2.7
5	CuO from preceding experiment treated as in experiment 1	....	....	.7
6	CuO from preceding experiment treated as in experiment 4	....	....	3.2

Experiments 4 and 6 show that both coarse and fine copper oxide, when partly reduced and reoxidized in air, retain nitrogen which is not completely removed at room temperature by evacuation and replacement with CO_2, 2.7 to 3.9 c. c. of nitrogen having been given off from 100 grams of oxide on subsequently heating it two hours at 850° C. in an atmosphere of CO_2.

On the other hand, when the CuO was subjected to alternate vacuum and CO_2 for several hours, at 850° C. instead of room temperature, until no further nitrogen was evolved, and was then cooled in CO_2, exposed to air, and again heated, as in experiments 4 and 6, the 40 to 100 mesh "wire" oxide gave off only 0.7 to 0.9 c. c. of nitrogen, whereas the 200-mesh material gave off 1.9 to 2.2 c. c.

It seems, then, that adsorption may account for the residual nitrogen, which varies in amount with the fineness of the oxide, and that the larger quantity of nitrogen obtained on the first vacuum-and-heat treatment subsequent to reoxidation in air of reduced copper is present in some form of chemical combination. The larger error due to the so-called chemically combined nitrogen can be eliminated from the Dumas method by first preparing the copper oxide that is subsequently mixed with the sample by heating it in a vacuum for several hours and cooling it in CO_2. The smaller but more persistent error due to adsorbed nitrogen can be reduced by using as coarse an oxide as possible.

When 50 grams of the 40 to 100 mesh CuO and coarse oxidized wire, both prepared as above, were used, the results were as follows, the time of heating being two hours:

Results of nitrogen determinations—40 to 100 mesh CuO and coarse oxidized wire used.

WITH SUCROSE.

Weight of sample.	Nitrogen.	Temperature.	Pressure.	Nitrogen.	Nitrogen.
Grams.	*C. c.*	*°C.*	*Mm. of Hg.*	*Mg.*	*Per cent.*
1.0000	0.4	25	740	0.43	0.04
1.0000	.1	26	745	.11	.01
1.0000	.14	30	744	.15	.02
WITH PICRIC ACID.					
0.2000	34.2	27	745	37.1	18.55
.2000	33.7	26	740	36.4	18.18
.2000	32.8	20	746	36.8	18.41
.2000	33.4	23	746	36.9	18.46

As the theoretical nitrogen content of picric acid is 18.34 per cent, both of these series show that the error is within the limits of the error of manipulation for most work.

In further corroboration, the explosives chemical laboratory of the bureau has made many nitrogen determinations on various nitro compounds with uniform success, by using these precautions in the preparation of the CuO.

In Table 10 and figure 5 are given the percentages of nitrogen obtained by the Dumas method in the previously described eight samples of coal.

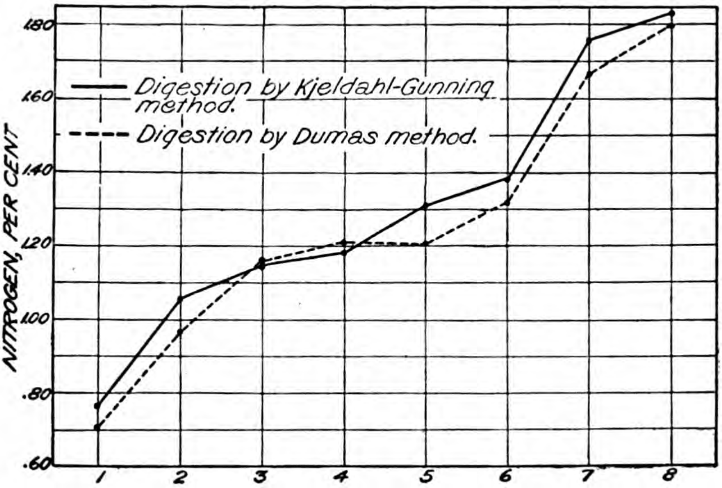

FIGURE 5.—Curves showing comparative results of determinations of nitrogen in various coals by the Dumas and by the Kjeldahl-Gunning method. Numbers on ordinates represent coals similarly numbered in Table 1.

TABLE 10.—*Comparative results of nitrogen determinations by Dumas and by Kjeldahl-Gunning method.*

Coal No.[a]	Determination No.—	Percentage of N by—		Difference.
		Dumas method.	Kjeldahl-Gunning method.	
1	1	0.73	0.77	−0.06
	2	.61		
	3	.80		
	Average	.71		
2	1	1.03	1.06	− .09
	2	.90		
	3	.97		
	Average	.97		
3	1	1.15	1.15	+ .01
	2	1.25		
	3	1.07		
	Average	1.16		
4	1	1.21	1.19	+ .02
5	1	1.29	1.31	− .10
	2	1.10		
	3	1.23		
	Average	1.21		
6	1	1.44	1.39	− .07
	2	1.19		
	3	1.32		
	Average	1.32		
7	1	1.61	1.76	− .09
	2	1.65		
	3	1.76		
	Average	1.67		
8	1	1.61	1.83	− .03
	2	1.86		
	3	1.83		
	4	1.91		
	Average	1.80		

[a] For a description of the coals see Table 1.

The procedure was the same as in the sucrose and picric acid determinations. The average values by the Dumas method check the Kjeldahl-Gunning values to within the total experimental error of the two methods. The larger deviation of the individual Dumas values are due to the experimental difficulty in burning a relatively large quantity of carbon as compared to the nitrogen present, without having the nitrogen contaminated with combustible gases, or leaving some unburned coal in the tube. These sources of error are not common to definite nitrogen compounds.

The volatile hydrocarbons of coal, including large amounts of methane, are given off readily on heating. These are slowly oxidized by CuO in the presence of CO_2[a], thereby making the results possibly too high.

Furthermore, coal and coke[b] oxidize very slowly by CuO in the presence of CO_2, a residue of unburned carbon possibly being left even after two or three hours of heating. So without examining the evolved nitrogen for combustible gases and the CuO residue for unburned carbon, there would always be some doubt of the accuracy of the individual determinations of the nitrogen in coals.

SUMMARY.

1. In determining the nitrogen content of eight different coals by various modifications of the Kjeldahl method, the highest and most concordant results in the shortest time of digestion were obtained by the combined Kjeldahl-Gunning method when both mercury and potassium sulphate were used as proposed by Dyer.[c] This confirms the results obtained on other organic materials by Sherman and Falk,[d] Gladding,[e] Wedemeyer,[f] Trescot,[g] and the committee on fertilizer analysis of the American Chemical Society.[h]

2. When 22 grams of potassium sulphate was used with 30 c. c. of acid, no losses occurred between limits of 7 and 15 grams of K_2SO_4 per 30 c. c. of H_2SO_4.

---

[a] Dunstan, W. R., and Carr, F. H., Note on a difficulty in the determination of nitrogen by the absolute method: Proc. Chem. Soc., vol. 12, 1896, pp. 48–49.

[b] Schmitz, G., Zur Bestimmung des Stickstoffes in Steinkohle und Koks: Ztschr. anal. Chem., Jahrg. 25, 1886, pp. 314–318.

[c] Dyer, B., Kjeldahl's method for the determination of nitrogen: Jour. Chem. Soc., vol. 67, 1895, pp. 811–817.

[d] Sherman, H. C., and Falk, M. J., The determination of nitrogen in organic compounds. Jour. Am. Chem. Soc., vol. 26, 1904, pp. 1469–1474.

[e] Gladding, T. S., Comparative work on nitrogen estimation by the Kjeldahl and Gunning methods and by a combination of the two methods: Proc. Assoc. Off. Agr. Chem., 1906, p. 85.

[f] Wedemeyer, K., Ein Wort zur Stickstoffbestimmung nach Kjeldahl-Gunning: Chem. Ztg., Jahrg. 22, 1898, p. 21.

[g] Trescot, T. C., Comparison of the Kjeldahl-Gunning-Arnold method with the official Kjeldahl and official Gunning method of determining nitrogen: Jour. Ind. Eng. Chem., vol. 5, 1913, pp. 914-915.

[h] The determination of nitrogen in commercial ammoniates of high nitrogen content. First report of the committee on nitrogen, division of fertilizer chemists, American Chemical Society: Jour. Ind. Eng. Chem., vol. 3, 1911, p. 691.

3. As a catalytic agent mercury proved more effective than copper sulphate, and for raising the boiling point of the mixture K_2SO_4 was superior to P_2O_5.

4. The official Gunning method did not prove applicable to coal, as the results from digestion for four hours were 0.2 to 0.3 per cent low.

5. Modifications for nitrates or nitro compounds did not give appreciably different results from those obtained with the ordinary Kjeldahl-Gunning method.

6. In no determination could low results be ascribed to the addition of potassium permanganate in the manner described. On the other hand, it seemed to promote higher results when the digestion was incomplete.

7. In all determinations, in order to insure a maximum yield of nitrogen, it was necessary to digest coal approximately two hours after the solution became colorless.

8. An independent check on the absolute accuracy of the Kjeldahl-Gunning method was obtained by determining the nitrogen in given samples by the Dumas gas-volumetric method. The greatest difference in the average values was 0.10 per cent and the mean difference was 0.05 per cent.

9. Errors in the Dumas method due to nitrogen from the fine CuO were minimized by previously heating the oxide for several hours in a vacuum and cooling it in CO_2, and using "wire-form" oxide pulverized to pass through a 40-mesh screen and to remain on a 100-mesh.

ACKNOWLEDGMENT.

The authors desire to acknowledge their obligations to G. A. Hulett, consulting chemist of the Bureau of Mines, for valuable suggestions and criticisms; to G. A. Burrell and his associates for making gas analyses; and to G. B. Taylor for making the special vacuum tests of experiment 7.

PUBLICATIONS ON FUEL TECHNOLOGY.

A limited supply of the following publications of the Bureau of Mines is temporarily available for free distribution. Requests for all publications can not be granted, and applicants should limit their selecting to publications that may be of especial interest to them. Requests for publications should be addressed to the director, Bureau of Mines, Washington, D. C.

Bulletin 1. The volatile matter of coal, by H. C. Porter and F. K. Ovitz. 1910, 56 pp., 1 pl., 9 figs.

Bulletin 2. North Dakota lignite as a fuel for power-plant boilers, by D. T. Randall and Henry Kreisinger. 1910. 42 pp., 1 pl., 7 figs.

Bulletin 3. The coke industry of the United States as related to the foundry, by Richard Moldenke. 1910. 32 pp.

Bulletin 4. Features of producer-gas power-plant development in Europe, by R. H. Fernald. 1910. 27 pp., 4 pls., 7 figs.

Bulletin 5. Washing and coking tests of coal at Denver, Colo., July 1, 1908, to June 30, 1909, by A. W. Belden, G. R. Delamater, J. J. Groves, and K. M. Way. 1910. 62 pp., 1 fig.

Bulletin 6. Coals available for the manufacture of illuminating gas, by A. H. White and Perry Barker, compiled and revised by H. M. Wilson. 1911. 77 pp., 4 pls., 12 figs.

Bulletin 7. Essential factors in the formation of producer gas, by J. K. Clement, L. H. Adams, and C. N. Haskins. 1911. 58 pp., 1 pl., 16 figs.

Bulletin 12. Apparatus and methods for the sampling and analysis of furnace gases, by J. C. W. Frazer and E. J. Hoffman. 1911. 22 pp., 6 figs.

Bulletin 13. Résumé of producer-gas investigations, October 1, 1904, to June 30, 1910, by R. H. Fernald and C. D. Smith. 1911. 393 pp., 12 pls., 250 figs.

Bulletin 14. Briquetting tests of lignite at Pittsburgh, Pa., 1908–9; with a chapter on sulphite-pitch binder, by C. L. Wright. 1911. 64 pp., 11 pls., 4 figs.

Bulletin 16. The uses of peat for fuel and other purposes, by C. A. Davis. 1911. 214 pp., 1 pl., 1 fig.

Bulletin 18. The transmission of heat into steam boilers, by Henry Kreisinger and W. T. Ray. 1912. 180 pp., 78 figs.

Bulletin 23. Steaming tests of coals and related investigations, September 1, 1904, to December 31, 1908, by L. P. Breckenridge, Henry Kreisinger, and W. T. Ray. 1912. 380 pp., 2 pls., 94 figs.

Bulletin 24. Binders for coal briquets, by J. E. Mills. 56 pp., 1 fig. Reprint of United States Geological Survey Bulletin 343.

Bulletin 27. Tests of coal and briquets as fuel for house-heating boilers, by D. T. Randall. 44 pp., 3 pls., 2 figs. Reprint of United States Geological Survey Bulletin 366.

Bulletin 28. Experimental work conducted in the chemical laboratory of the United States fuel-testing plant at St. Louis, Mo., January 1, 1905, to July 31, 1906, by N. W. Lord. 51 pp. Reprint of United States Geological Survey Bulletin 323.

Bulletin 29. The effect of oxygen in coal, by David White. 80 pp., 3 pls. Reprint of United States Geological Survey Bulletin 382.

Bulletin 31. Incidental problems in gas-producer tests, by R. H. Fernald, C. D. Smith, J. K. Clement, and H. A. Grine. 29 pp., 8 figs. Reprint of United States Geological Survey Bulletin 393.

Bulletin 32. Commercial deductions from comparisons of gasoline and alcohol tests of internal-combustion engines, by R. M. Strong. 38 pp. Reprint of United States Geological Survey Bulletin 392.

Bulletin 33. Comparative tests of run-of-mine and briquetted coal on the torpedo boat *Biddle*, by W. T. Ray and Henry Kreisinger. 50 pp., 10 figs. Reprint of United States Geological Survey Bulletin 403.

Bulletin 34. Tests of run-of-mine and briquetted coal in a locomotive boiler, by W. T. Ray and Henry Kreisinger. 33 pp., 9 figs. Reprint of United States Geological Survey Bulletin 412.

Bulletin 35. The utilization of fuel in locomotive practice, by W. F. M. Goss. 29 pp., 8 figs. Reprint of United States Geological Survey Bulletin 402.

Bulletin 36. Alaskan coal problems, by W. L. Fisher. 1911. 32 pp., 1 pl.

Bulletin 39. The smoke problem at boiler plants, a preliminary report, by D. T. Randall. 31 pp. Reprint of United States Geological Survey Bulletin 334, revised by S. B. Flagg.

Bulletin 40. The smokeless combustion of coal in boiler furnaces, with a chapter on central heating plants, by D. T. Randall and H. W. Weeks. 188 pp., 40 figs. Reprint of United States Geological Survey Bulletin 373, revised by Henry Kreisinger.

Bulletin 43. Comparative fuel values of gasoline and denatured alcohol in internal-combustion engines, by R. M. Strong and Lauson Stone. 1912. 243 pp., 3 pls., 32 figs.

Bulletin 49. City smoke ordinances and smoke abatement, by S. B. Flagg. 1912. 55 pp.

Bulletin 54. Foundry cupola gases and temperatures, by A. W. Belden. 1913. 29 pp., 3 pls., 16 figs.

Bulletin 55. The commercial trend of the producer-gas power plant in the United States, by R. H. Fernald. 1913. 93 pp., 1 pl., 4 figs.

Bulletin 56. First series of coal-dust tests in the experimental mine, by G. S. Rice, L. M. Jones, J. K. Clement, and W. L. Egy. 1913. 115 pp., 12 pls., 28 figs.

Bulletin 58. Fuel-briquetting investigations, July, 1904, to July, 1912, by C. L. Wright. 1913. 277 pp., 21 pls., 3 figs.

Bulletin 76. United States coals available for export trade, by Van. H. Manning. 1914. 15 pp., 1 pl.

Bulletin 82. International conference of mine experiment stations, Pittsburgh, Pa., September 14–21, 1912, compiled by G. S. Rice. 1914. 99 pp.

Bulletin 88. The condensation of galsoline from natural gas, by G. A. Burrell, F. M. Seibert, and G. G. Oberfell. 1915. 106 pp., 6 pls., 18 figs.

Technical Paper 1. The sampling of coal in the mine, by J. A. Holmes. 1911. 18 pp., 1 fig.

Technical Paper 2. The escape of gas from coal, by H. C. Porter and F. K. Ovitz. 1911. 14 pp., 1 fig.

Technical Paper 3. Specifications for the purchase of fuel oil for the Government, with direction for sampling oil and natural gas, by I. C. Allen. 1911. 13 pp.

Technical Paper 5. The constituents of coal soluble in phenol, by J. C. W. Frazer and E. J. Hoffman. 1912. 20 pp., 1 pl.

Technical Paper 8. Methods of analyzing coal and coke, by F. M. Stanton and A. C. Fieldner. 1913. 42 pp., 12 figs.

Technical Paper 10. Liquefied products of natural gas; their properties and uses, by I. C. Allen and G. A. Burrell. 1912. 23 pp.

Technical Paper 16. Deterioration and spontaneous combustion of coal in storage; a preliminary report, by H. C. Porter and F. K. Ovitz. 1912. 14 pp.

Technical Paper 20. The slagging type of gas producer, with a brief report of preliminary tests, by C. D. Smith. 1912. 14 pp., 1 pl.

Technical Paper 25. Methods for the determination of water in petroleum and its products, by I. C. Allen and W. A. Jacobs. 1912. 13 pp., 2 figs.

Technical Paper 31. Apparatus for the exact analysis of flue gas, by G. A. Burrell and F. M. Seibert. 1913. 12 pp., 1 fig.

Technical Paper 35. Experiments with furnaces for a hand-fired return tubular boiler, by S. B. Flagg, G. C. Cook, and F. E. Woodman. 1914. 32 pp., 1 pl., 4 figs.

Technical Paper 35. Weathering of the Pittsburgh coal bed at the experimental mine near Bruceton, Pa., by H. C. Porter and A. C. Fieldner. 1914. 35 pp., 14 figs.

Technical Paper 37. Heavy oil as fuel for internal combustion engines, by I. C. Allen. 1913. 36 pp.

Technical Paper 38. Wastes in the production and utilization of natural gas, and methods for their prevention, by Ralph Arnold and F. G. Clapp. 1913. 29 pp.

Technical Paper 45. Waste of oil and gas in the Mid-Continent fields, by R. S. Blatchley. 1914. 54 pp., 2 pls., 15 figs.

Technical Paper 49. The flash point of oils, methods and apparatus for its determination, by I. C. Allen and A. S. Crossfield. 1913. 31 pp., 2 figs.

Technical Paper 50. Metallurgical coke, by A. W. Belden. 1913. 48 pp., 1 pl., 23 figs.

Technical Paper 55. The production and use of brown coal in the vicinity of Cologne, Germany, by C. A. Davis. 1913. 15 pp.

Technical Paper 57. A preliminary report on the utilization of petroleum and natural gas in Wyoming, by W. R. Calvert, with a discussion of the suitability of natural gas for making gasoline, by G. A. Burrell. 1913. 23 pp.

Technical Paper 63. Factors governing the combustion of coal in boiler furnaces; a preliminary report, by J. K. Clement, J. C. W. Frazer, and C. E. Augustine. 1914. 46 pp., 26 figs.

Technical Paper 65. A study of the oxidation of coal, by H. C. Porter. 1914. 30 pp., 12 figs.

Technical Paper 74. Physical and chemical properties of the petroleums of California, by I. C. Allen, W. A. Jacobs, A. S. Crossfield, and R. R. Mathews. 1914. 38 pp., 1 fig.

Technical Paper 76. Notes on the sampling and analysis of coal, by A. C. Fieldner. 1914. 59 pp., 6 figs.

Technical Paper 80. Hand firing soft coal under power-plant boilers, by Henry Kreisinger. 1915. 83 pp., 32 figs.

Technical Paper 89. Coal-tar products and the possibility of increasing their manufacture in the United States, by H. C. Porter, with a chapter on coal-tar products used in explosives, by C. G. Storm. 1915. 21 pp.

Technical Paper 97. Saving fuel in heating a house, by L. P. Breckinridge and S. P. Flagg. 1915. 35 pp., 3 figs.

Technical Paper 104. Analyses of natural gas and illuminating gas by fractional distillation at low temperatures and pressures. 1915. 41 pp., 7 figs.

Technical Paper 109. Composition of the natural gas used in 25 cities, with a discussion of the properties of natural gas, by G. A. Burrell and G. G. Oberfell. 1915. 22 pp.

Technical Paper 115. Inflammability of mixtures of gasoline vapor and air, by G. A. Burrell and H. T. Boyd. 1915. 18 pp., 2 figs.

Technical Paper 120. A bibliography of the chemistry of gas manufacture, by W. F. Rittmann, M. C. Whitaker, and M. S. Howard. 1915. 29 pp.

Technical Paper 124. Notes on the use of low-grade fuel in Europe, by R. H. Fernald. 1915. 37 pp.

○